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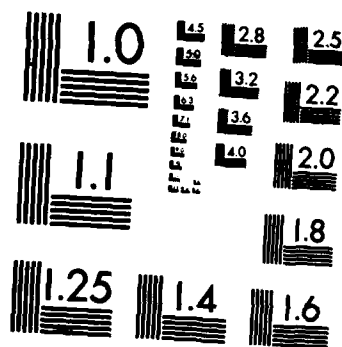
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRONIC PROMOTERS AND SEMICONDUCTOR OXIDATION: Co and Na on Si(111) SURFACES ALKALI METALS		5. TYPE OF REPORT & PERIOD COVERED Interim; 8/1/84-7/30/86
7. AUTHOR(s) A. Franciosi, P. Philip, S. Chang, A. Wall, A. Raisanen, N. Troullier, and P. Soukiassian (University of Wisconsin-Madison)		6. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0545		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS task NR 372-162
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Minnesota 1919 University Ave St. Paul, MN 55104		12. REPORT DATE 4/25/86
10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Electronics Division (Dr. K. Hathaway) Department of the Navy, Arlington, VA 22217		13. NUMBER OF PAGES 19
11. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		14. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; unlimited distribution		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTE S NOV 19 1986 D		
18. SUPPLEMENTARY NOTES Submitted for publication to Physical Review B		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Interface reactivity; Catalysis; Metal-semiconductor interfaces		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We examine the effect of thin (1-2 monolayers) overlayers of the low-electronegativity metals Cs and Na on the oxidation of Si(111) cleavage surfaces. Synchrotron radiation photoemission studies of oxygen chemisorption as a function of overlayer thickness and oxygen exposure indicate large oxidation promotion effects and the formation of Si-oxide phases where high Si-oxidation states dominate. Comparison with promotion effects induced by transition metals and noble metals overlayers forces a		

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ELECTRONIC PROMOTERS AND SEMICONDUCTOR OXIDATION:

ALKALI METALS ON Si(111) SURFACES

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Abstract

We examine the effect of thin (1-2 monolayers) overlayers of the low-electronegativity Cs and Na metals on the oxidation of Si(111) cleavage surfaces. Synchrotron radiation photoemission studies of oxygen chemisorption as a function of overlayer thickness and oxygen exposure indicate large oxidation promotion effects and the formation of Si-oxide phases where high Si-oxidation states dominate. Comparison with promotion effects induced by transition metal and noble metal overlayers forces for alkali metals a re-evaluation of the microscopic mechanisms proposed to explain overlayer-induced oxidation promotion.

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Many metal overlayers on semiconductor surfaces give rise to oxidation promotion effects upon exposure to atomic or molecular oxidizing species¹⁻⁹. Most mechanisms proposed to explain oxidation promotion for silicon¹⁻⁹ are based on one or more of the following aspects: disruption of the semiconductor surface⁴, "metallization" of the surface^{5,10}, disruption of the Si sp³ hybridization³⁻⁵, formation of low-stability interface alloys^{3,5} with substantial catalytic activity for dissociating molecular species^{5,6}.

To clarify the relative importance of these mechanisms, we have conducted a study of the oxidation of Si(111) surfaces in the presence of Cs and Na overlayers. These metals represent important test cases since they do not appear to give rise to substantial surface disruption or interdiffusion¹¹⁻¹⁵, and they exhibit a well-defined transition from a non-metallic to a metallic state at coverages on the order of 0.5 monolayers¹²⁻¹⁶. Furthermore a number of stimulating pioneering studies have shown that co-adsorption of Cs and oxygen on metals¹⁷ and GaAs⁶ may enhance the oxidation kinetics.

In the case of both Cs and Na overlayers we observe a strong oxidation promotion effect that is not related to the formation of low stability silicide-like phases at the interface, nor to the metallization¹⁵ of the silicon surface, so that electrostatic overlayer-oxygen interactions mediated by the substrate should be examined to explain catalytic promotion¹⁸.

All experiments were performed at room temperature following the methodology described in refs. 8-9 and 19-20, at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Most of our data for Cs have been obtained at saturation coverage¹²⁻¹⁵ (~ 1 monolayer). For Na, we have selected the monolayer coverage range for consistency. The results are summarized in angular integrated energy distribution curves (EDC's) in figs. 1-3. The results for the Si 2p core

emission in fig. 2 are shown after subtraction of a smooth secondary background, correction for substrate band bending and (approximate) normalization to the main emission feature, in order to emphasize lineshape changes.

Results for the valence band emission from the Si (111)-Cs system are shown in fig. 1. The bottom-most spectrum is representative of the clean Si(111) surface emission, while spectra displaced upward show the effect of the deposition of one monolayer of Cs followed by sequential exposure to oxygen. The valence band emission for Si(111)-Cs before oxidation is in good agreement with the results of Tochiwara et al.¹⁴, with a sharp emission feature at about 1 eV and the shallow 5p core levels between 10 and 15 eV. Correspondingly, the Si(111)-Cs system shows no interdiffusion, a strongly polar chemisorption bond that lowers the semiconductor surface work function and, near saturation coverage, a "tailing" of valence states up to E_F (fig. 1) and metallic-like plasmon loss features^{12-14,20}.

Exposures as low as 0.25 L in fig. 1 suppress the emission from the 1eV features - which are related to localized Cs-Si bonding states²⁰ - and give rise to a broad, structured oxide-related emission band centered about 6eV below E_F . Emission from the shallow Cs 5p cores does not appear attenuated upon oxidation, while a definite broadening of the 5p lineshape progressively takes place. Further oxygen exposure yields little change of the valence band emission. At oxygen exposures up to 100L a further decrease of the semiconductor-derived emission within 4eV of E_F is observed, but the valence band remains dominated by the 6eV oxide emission band and by the Cs 5p cores.

Results for the valence band emission from Si-Na are not shown here due to space limitations, but they are qualitatively similar to those of fig. 1. Very

little is known of Si-Na interfaces²⁰, and we will draw on Si-K results¹¹⁻¹⁶ in discussing our data because of the electronic similarity of Na and K. A recent paper by Ciraci and Batra¹⁵ discuss the Si(100)-K case, and a number of analogies are found with the Si(100)-Cs and Si(111)-Cs cases. A saturation coverage on the order of one monolayer is observed, together with a clear 2x1 LEED pattern and a decrease of the work function. The occurrence of metallic behavior at metal coverages above 0.5 monolayers also seems a common characteristic of alkali metal overlayers¹²⁻¹⁶. It was concluded in ref. 15 that the metallic character attributed to the overlayer corresponds, in fact, to the "metallization" of the Si surface through charge transfer, and that the overlayer-substrate bonding is ionic at all metal coverages¹⁵. Whatever the validity of this model for other Si-alkali metal systems, we observe no interdiffusion at the interface, and a strongly polar chemisorption bond in the Si(111)-Na case²⁰.

In fig. 2 we show the effect of oxygen exposure on the Si 2p lineshape for a number of Si-metal systems. Spectra for Sm (1.5 ML), Cs (1ML), Na (1.5 ML) and Cr (2 ML) overlayers on Si(111) are shown before (dashed line) and after (solid line) exposure to 100 L of oxygen (24L for Cs). For comparison we also show (bottom-most spectrum) results for the oxidation of the free Si(111) surface. The overlayers included in fig. 2 are those which exhibit the largest oxidation promotion activity observed to date¹⁻⁹ on Si. We have chosen comparable metal coverages for all overlayers, although for Sm and Cr we have selected slightly larger values in order to exceed the critical coverage for oxidation promotion (about 2.5Å for Sm⁹ and 1.5Å for Cr⁸). Below this coverage the two overlayers exhibit little catalytic activity⁸⁻⁹. The vertical bars in fig. 2 at 0.9, 1.8, 2.6 and 3.5 eV mark the position of the chemically shifted Si 2p contributions observed by Hollinger and Himpsel²¹ during Si(111) oxidation, and associated by

these authors with Si atoms bonded to 1, 2, 3, and 4 oxygen atoms, respectively. Vertical bar α marks the position of the dominant Si 2p oxide feature observed by Riedel et al.²² during oxidation of amorphous silicon.

If we focus now on the results for Cs and Na overlayers, we note that the unoxidized Si 2p spectra (dashed line) show high binding energy features. A broad tail extends from 1.2 eV to 3.0 eV in the case of Cs overlayers, while a well-resolved feature is observed between 2 and 3.5 eV for Na overlayers. We associate these features with 2p emission channels that involve collective excitations^{14,20}. Upon oxidation fig. 2 shows that both Cs and Na overlayers exhibit oxidation promotion activity, that the magnitude of the promotion effect is larger for Cs than for Na, and that the reaction products involve several non-equivalent oxidation states for silicon, with high oxidation states being predominant. The nature of the reaction products appears similar to that observed in the presence of Sm and Cr overlayers, and consistent with what could be expected for a disordered, substoichiometric SiO₂ surface phase²². A rough estimate²⁰ of the amount of Si that appears oxidized when Cs overlayers are exposed to 24L of oxygen can be made on the basis of the intensity ratio of the oxidized and unoxidized Si 2p lines²⁰, and suggests that 3-7 layers of silicon have reacted to form the surface oxide. We mention that no saturation of oxygen adsorption was observed in the 10⁻¹-10³L exposure range²⁰, and that exposures as small as 1L give rise to well-defined oxidized Si features.

Several microscopic mechanisms have been proposed to explain overlayer-induced silicon oxidation promotion. Most models²⁻⁵ propose that the formation of interface reaction products breaks the sp³ configuration of the silicon substrate so that the Si atoms at the interface would be in an amorphous metallic environment with "disrupted bonds"² and they could easily be oxidized². Abbati

et al.⁵ explain the lack of adsorption saturation effects by proposing a self-sustaining mechanism in which a flow of Si atoms is established through a silicon-metal intermixed layer located between the growing oxide and the Si substrate. This layer would make Si atoms with "broken"⁵ sp^3 configuration and "weaker" Si-Si bonds available for oxidation. The incoming oxygen would then react preferentially with Si and displace the metal from Si so that the metal would become available for intermixing with the substrate and produce further Si disruption⁵. Cros³ points out that the increased density of states at E_F in the intermixed silicon-metal interface species would ease the breaking of the oxygen molecule and the creation of atomic oxygen excited states³.

In our view one of the experimental observations that most strongly supports the "reactive interface" picture²⁻⁵ of oxidation promotion is the evidence of a critical coverage for oxidation promotion due to Cr and Sm overlayers⁸⁻⁹. Both overlayers show substantial catalytic activity only for metal coverages above a critical threshold coverage that corresponds to the onset of Si-metal interdiffusion and to the formation of silicide-like interface species. The results in fig. 2, however, provide definitive evidence against the general applicability of this microscopic picture. Both Cs and Na overlayers are found to give rise to large oxidation promotion effects although they do not intermix with silicon, they do not form silicide-like surface species, and they do not break the sp^3 hybridization of the Si surface atoms.

An alternative mechanism could involve the "metallization" of the Si surface^{10,15} without disruption of the Si-surface and breaking of the Si sp^3 hybridization. Okuno et al.¹⁰ had proposed that "tailing" of the metal-wavefunction into the semiconductor may "screen" Coulomb interaction and reduce the stability of the semiconductor covalent bonding. Although this picture was

rather qualitative¹⁰, calculations by Ciraci and Batra¹⁵ show that toward saturation coverage for K overlayers on Si(111) the adatom-substrate distance becomes smaller and results in an effective core screening¹⁵ in agreement with work function data. We sought to investigate this second microscopic picture by studying in fig. 3 the evolution of the characteristic overlayer-induced collective excitations as a function of oxygen exposure. Upon deposition of Na on the Si(111) surface, well-defined loss features are observed on the high binding energy side of the Si 2p and Na 2p core lines. Such "interface plasmons"²⁰ are a direct manifestation of the overlayer-induced metallization¹⁵ of the surface. Upon oxidation the results of figs. 2 and 3 indicate that Na-induced oxidation promotion effects are encountered in a wide range of oxygen exposures, although the characteristic metallic surface loss feature disappears in the early chemisorption stage.

Another aspect of alkali-metal chemisorption, namely the establishment of a substantial surface dipole, may instead play a role in explaining oxidation promotion effects induced by alkali metals. The chemisorption of alkali metals induces a modification of the electrostatic potential in the surface region¹⁶: the alkali valence electrons are polarized^{15,18} toward the substrate surface leading to a dipole layer which raises the electron levels of the "metallized" silicon surface relative to the vacuum level. The rigid shift of the Fermi level yields the measured reduction of the work function. If a molecular species is absorbed within the surface dipole layer, the energy shift of the molecular level is less pronounced than that of the substrate levels. This may result in a relative shift to higher binding energies of the molecular levels relative to E_F , charge transfer to molecular antibonding orbitals, and formation of atomic oxygen that can react with Si atoms in the interface region. This mechanism was

verified by Wimmer et al.¹⁸ for K and CO co-adsorption on Ni, and its extension to the Si-O₂ case is only tentative and based on the following points: 1) Alkali metal chemisorption does induce a "metallization" of the Si surface and 2) establishes a surface dipole layer as shown by the decrease in work function. 3) A quantitative analysis of the variation of Cs, Na, and Si core level emission intensity with oxygen chemisorption indicates that oxides are nucleated below the alkali-metal monolayer^{20,23}. This can be seen for example in fig. 1 where the emergence of the oxide band and the corresponding attenuation of the Si valence band emission are not accompanied by detectable attenuation of the Cs 5p emission. In contrast, for a number of noble and transition metal overlayers on Si^{1,4,8} it appears that Si-oxide species nucleate on top of the silicide-like metallic surface layer²⁵. 4) The model is consistent with the reduced activity of Na overlayers relative to Cs overlayers in promoting oxidation: because of the higher electronegativity of Na relative to Cs the chemisorption-induced surface dipole is expected to be reduced in the case of Na. Furthermore, the reduced Na radius relative to Cs would make the location of chemisorbed molecular species within the surface dipole layer less likely for Na overlayers than for Cs overlayers²⁴.

This work was supported by ONR under grant N00014-84-K-0545 and the Micro-electronics and Information Sciences Center of the University of Minnesota. One of us (P.S.) would like to acknowledge the support of the NATO International Visiting Scientist Program. The Synchrotron Radiation Center of the University of Wisconsin-Madison is supported by NSF and we gratefully acknowledge the cheerful support of its staff.

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20. A more complete analysis will be given in a longer forthcoming paper: P. Philip, S. Chang, A. Wall, A. Raisanen, N. Troullier, A. Franciosi, and P. Soukiassian, to be published.
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23. Early results for Cs and O co-adsorption on metals¹⁷ and Si(100) surfaces" were interpreted as suggesting the formation of a Cs-O- substrate double layer.
24. We mention that Su et al.⁶ have proposed that dissociative chemisorption of O₂ on top of a Cs overlayer could explain Cs-induced oxidation promotion effects on GaAs(110). The relative importance of the surface dipole layer, surface metallization and overlayer morphology in the case of GaAs is more difficult to assess in the absence of a theoretical background^{15-16,18}.
25. Since the oxide layer is formed underneath the metal overlayer, one could argue that oxidation should slow down rapidly because of the decrease in the electric dipole field with increasing layer thickness, until no more oxidation activity could take place. It is likely, though, that the Cs-Si surface dipole field responsible for the initial oxidation promotion is replaced in the following stages by an equally effective Cs-O surface dipole, as demonstrated by the lack of major changes in the Cs 5p binding energy in fig. 1. In this connection we have to emphasize that we have no data for exposures greater than 10³L, so that saturation may indeed take place at higher exposures, and that inhomogeneities in the thickness of the oxide layer may also play a role.

FIGURE CAPTIONS:

Figure 1. Valence band emission from the Si(111)-Cs interface as a function of oxygen exposure. The bottom-most spectrum shows the clean Si(111) emission. Spectra displaced upward show the effect of monolayer Cs deposition followed by sequential oxygen exposure.

Figure 2. Si 2p core emission before (dashed line) and after (solid line) exposure to 100L (24L for Cs) of oxygen. We show results for the free Si surface (bottom-most EDC) while spectra displaced upward show the effect of Cr, Na, Cs and Sm overlayers on Si oxidation. The vertical bars mark the position of Si 2p oxide features associated by Hollinger and Himpsel²¹ with Si atoms coordinated with one, two, three and four oxygen atoms. Vertical bar α marks the position of a Si 2p oxide feature identified by Riedel et al. (ref. 22) during oxidation of amorphous silicon.

Fig. 3. Emission from the Si 2p and Na 2p core levels from a 1.5 ML Na overlayer on Si(111). The bottom-most spectra show the situation before Na deposition. Spectra displaced upward show the effect of Na deposition and of the following exposure to 0.1 and 1.0L of oxygen. Collective loss features visible on the high binding energy side of the core lines reflect the overlayer-induced metallization of the semiconductor surface. These characteristic loss features are suppressed in the early stages of oxygen chemisorption (top-most spectrum).

PHOTOELECTRON INTENSITY (ARB. UNITS)

Si (III) : Cs-O₂
Valence Band

$h\nu = 80$ eV

1.0 L

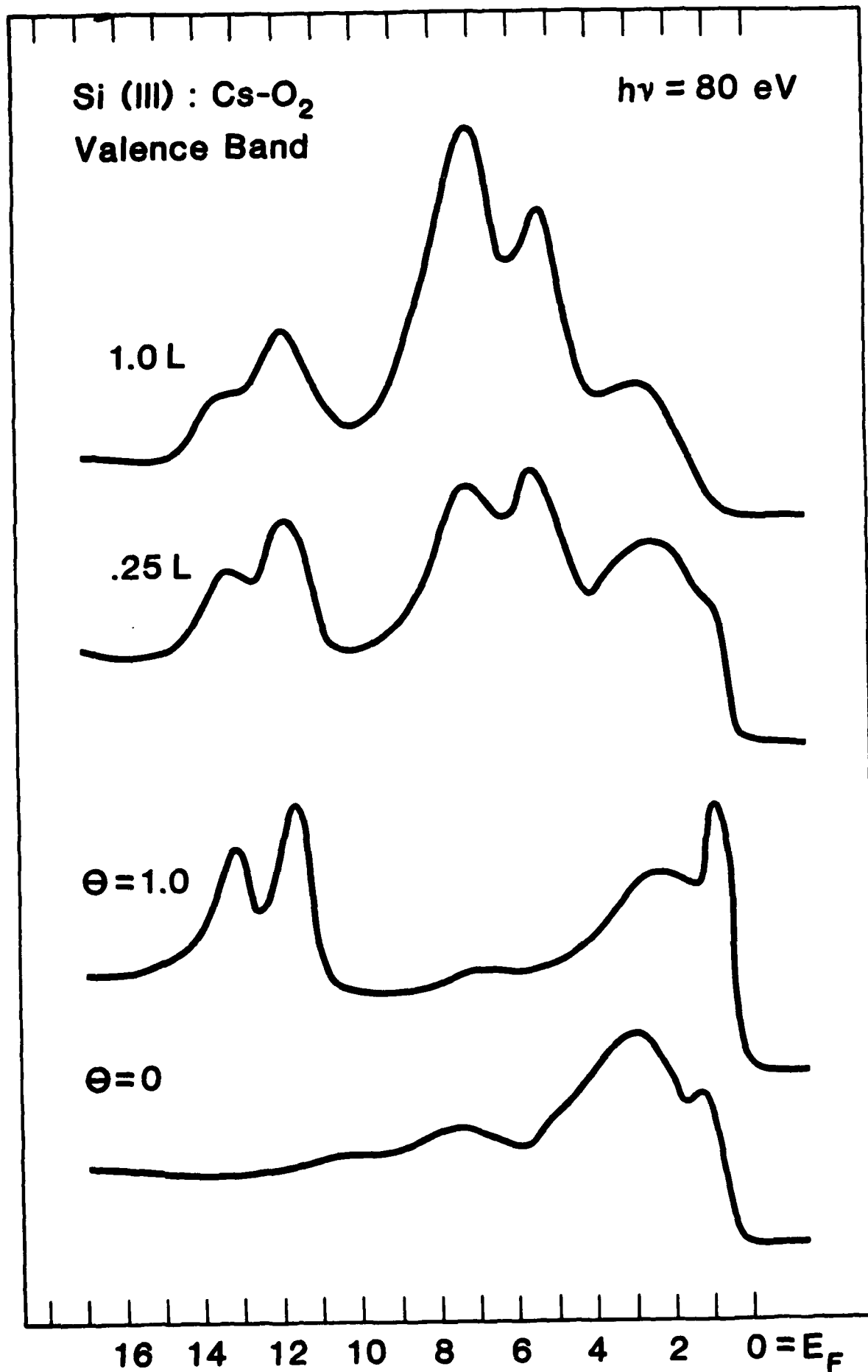
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$\Theta = 1.0$

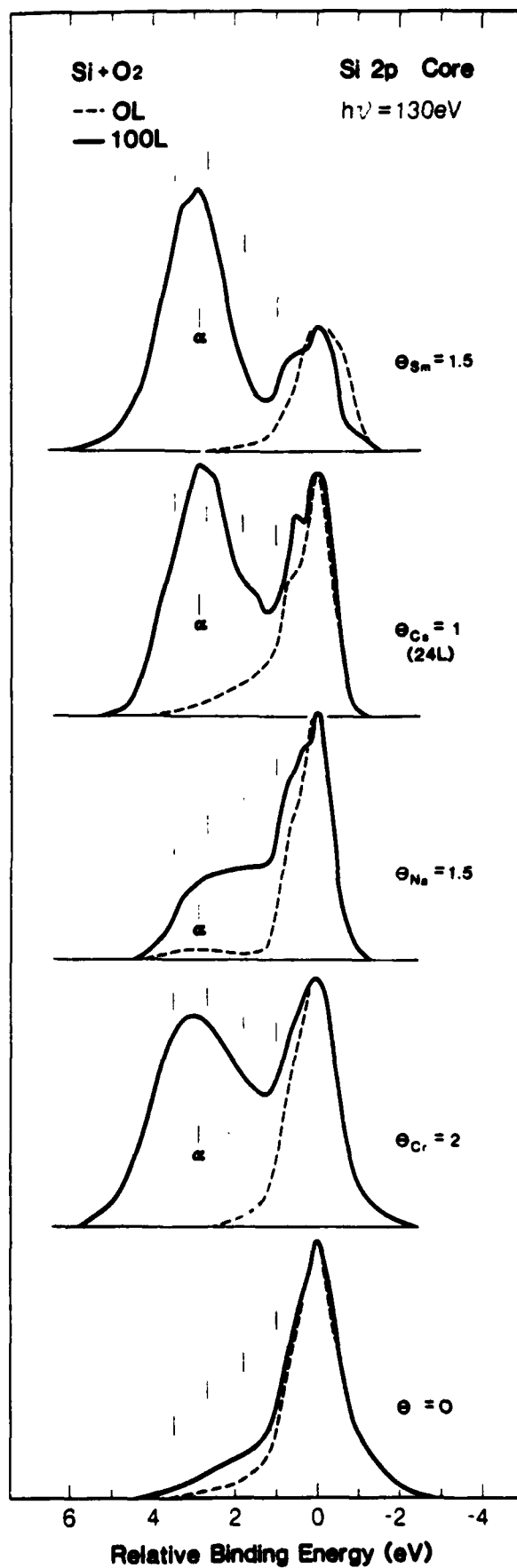
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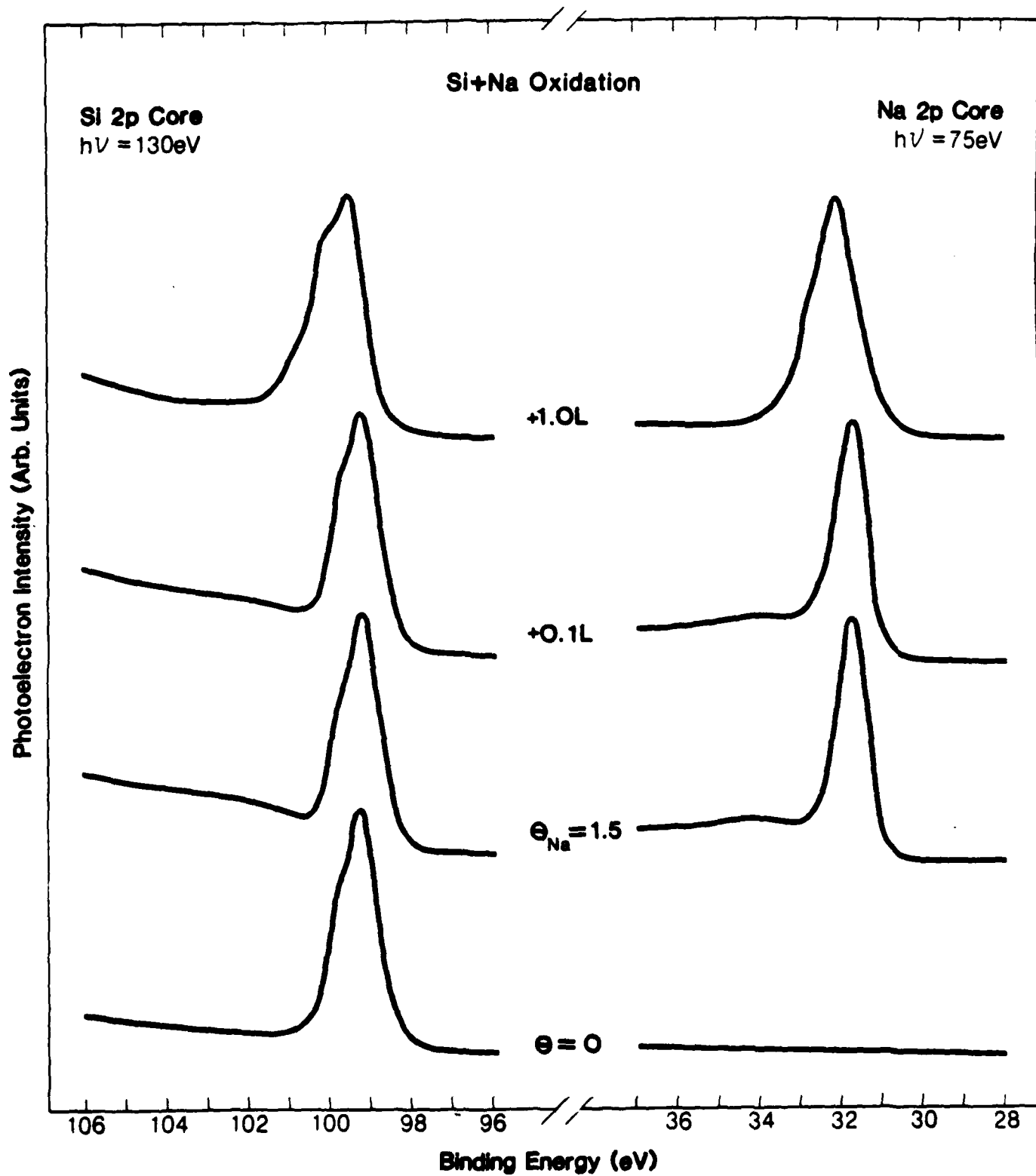
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BINDING ENERGY (eV)



Photoelectron Intensity (Arb. Units)





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